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The Formation of Conducting Gold Films by Thermal Decomposition and Direct Patterning  
Using Electron Beam Lithography of the Gold Cluster  $\text{Au}_{55}[\text{P}(\text{C}_6\text{H}_5)_3]_{12}\text{Cl}_6$

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(6 December, 1993)

ABSTRACT

In this paper we present the fabrication and electrical conductivities of conducting gold cluster films. The films are deposited onto a  $\text{Si}_3\text{N}_4$  substrate from a gold cluster solution by spin coating. After thermal decomposition and annealing at  $180^\circ\text{C}$ , a granular gold film with a resistivity of about  $10^{-6}\Omega\text{-m}$  is formed. Resistivity measurements as a function of temperature show a low residual resistivity ratio. The low temperature resistivity indicates an electron mean-free-path close to the cluster diameter, and the temperature dependent resistivity is found to be in agreement with the Bloch-Grüneisen model. The spin coated gold cluster film also acts as a negative electron beam resist. Fine structures as small as  $0.1\mu\text{m}$  can be patterned directly by electron beam exposure. The electron beam exposed structures were found not to be conducting even after chemical extraction and firing.

## §1. INTRODUCTION

Vacuum evaporation, sputtering and chemical vapor deposition are the most widely used techniques for thin metal film deposition, which has long been an important subject due to its considerable applications, especially in the field of microelectronics. Recently, extensive studies have been performed on ion (Ohmura et. al 1987, Harriot et. al 1986, Mantese et. al 1988), laser (Gupta and Jagannathan 1987, Gross et. al 1987), and electron beam (Craighead and Schiavone 1986, Lee and Hatzakis 1989, Mantese et. al 1988) induced decomposition of solid organometallic films and gas phase precursors for the purpose of direct patterning metallic and high  $T_c$  superconducting films. Usually, these techniques involve many steps, require a vacuum system, and a gas handling system. Also, the diffraction limit and thermal diffusion due to the decomposition sources make the fabrication of structures with lateral dimensions much below the micron scale difficult. In this paper we present a straightforward way to use a spin coated gold compound film for the production of conducting gold films by thermo-decomposition. We also show that the gold cluster film acts as a negative electron beam resist allowing direct patterning of submicron scale gold structures by electron beam lithography.

The gold cluster  $\text{Au}_{55}[\text{P}(\text{C}_6\text{H}_5)_3]_{12}\text{Cl}_6$  was used in this work. This compound is air stable and soluble in dichloromethane, but decomposes on warming in the solid state as well as in solution to give metallic gold and  $\text{Au}[\text{P}(\text{C}_6\text{H}_5)_3]\text{Cl}$  (Schmid 1990). It is known from the mass spectra (EI) of metal clusters such as  $[\text{Ru}_4(\text{CO})_{10}\text{Cl}_2(\text{OMe})(\text{OH})]$  (Eady et. al 1997) and  $[\text{Pt}_5(\text{CO})_6(\text{PEt}_3)_4]$  (Wurminghausen et. al 1980) that under electron bombardment the metal cluster decomposes with a loss of the ligand. Therefore, it was expected that electron beam or UV irradiation of a  $\text{Au}_{55}[\text{P}(\text{C}_6\text{H}_5)_3]_{12}\text{Cl}_6$  thin film should result in decomposition of the gold cluster

to form a metallic gold film.

## §2. EXPERIMENTAL

The gold compound was prepared by reduction of  $\text{Au}[\text{P}(\text{C}_6\text{H}_5)_3]\text{Cl}$  by  $\text{BH}_3$  in dry benzene following the equations (Schmid 1990).



The gold compound was purified by dissolving in dichloromethane and filtering to separate small amounts of insoluble matter, and then filtered a second time, through Celite to remove any traces of colloidal gold. Pentane was then added to the dichloromethane solution to precipitate the solid. Finally, the precipitate was collected and vacuum dried as black solid. Precise details of the preparation are given elsewhere (Yan et. al 1994).

A solution of the compound was prepared by dissolving 20mg of the black solid in 0.25mL of dichloromethane and 0.25mL of dichloroethane followed by centrifugation to remove any insoluble materials. Immediately after preparation the gold compound solution was spin coated onto a  $\text{Si}_3\text{N}_4$  coated substrate to form a black film. For the thermal decomposition the wafer was transferred into a conventional oven and baked at  $110^\circ\text{C}$  for an hour. The baked wafer

was then developed in dichloromethane for 10sec and a brown gold compound film was formed on the substrate. Further thermal annealing was carried out by baking sample at 180°C for another hour. At each step a scanning electron microscope was used to study the gold grain size. A diamond stylus was used to scribe the film to define a four-terminal structure about 1mm wide and 5mm long for resistivity measurements at low temperatures. After scribing the film it was mounted on a copper holder and the electrical contacts were made with thin gold wire attached to the sample with silver paint. The holder and sample were attached to a pumped He<sup>4</sup> cryostat using silver paint to ensure a good thermal contact to the sample. A standard ac bridge technique was used to measure the resistance at temperatures ranging from 295 to 1.4K.

The procedure of direct patterning was as follows. First, a Si<sub>3</sub>N<sub>4</sub> coated substrate was spin coated with the gold compound solution at 1500rpm for 25sec. Without baking, the wafer was loaded into a scanning electron microscope modified for lithography (Nabity and Wybourne 1989). To determine the optimal exposure conditions, test patterns were exposed with 40kV electrons at different dosages. The exposed samples were developed by dipping them in dichloromethane at 22°C for 15sec, followed by a 15sec rinse in 2-propanol, and they were finally blow dried with a stream of dry nitrogen gas.

For the purpose of electrical resistivity measurements, a micron size four-terminal wire shaped structure was fabricated using electron beam lithography. The electrical measurements on this sample were carried out at room temperature using a four terminal probe station.

In an attempt to increase the electrical conductivity of the micron scale structures, chemical extraction was done to try to remove any organic materials from the electron beam exposed structures. First, the sample was boiled with dichloromethane for several hours to

remove any dichloromethane soluble material. The sample was then heated at about 120°C under a vacuum of 0.1mbar for several hours to remove any sublimable materials. Finally, the sample was extracted by boiling in water for several hours to remove any water soluble inorganic salts. Standard firing procedures were also performed under vacuum as well as in the air at temperatures ranging from 200 to 600°C to remove any organic/inorganic materials.

At all stages of film preparation and subsequent treatment, compositional analysis by electron probe microanalysis (EPMA) was used to diagnose the gold concentration by weight. The concentrations were compared with the weight concentration expected from the molecular formula, as shown in Table 1.

### §3. RESULTS

#### 3.1. Thermal decomposition

Figure 1a is a micrograph of the thermally decomposed film, which shows a granular size in the order of 20nm which is much larger than the gold cluster size (Schmid et. al 1988). We are confident these granules are indeed gold since the EPMA showed the weight percentage of gold in the film to increase from 79% to 96% on thermal decomposition (Table 1). From the micrographs, the thickness of the thermally decomposed film was estimated to be on the order of the grain size. Electrical measurements on the thermally decomposed film at room temperature showed a very high resistivity. Taking the width of the film to be the apparent physical width 1mm, the resistivity was greater than  $10^2 \Omega\cdot m$ . Such a high resistivity is probably due to either noncontiguous gold clusters, or to chemical residue surrounding the gold clusters. From the electron micrographs we were unable to distinguish between the two possibilities. As expected,

when the film was annealed at 180°C for an hour, the small gold granules coalesced to form bigger granules with an average grain size of 60nm, as shown in Fig.1b. The annealing increased the weight percentage of gold in the film from 96% to 97%. After annealing the effective width of the film was estimated from micrographs to be about 66% of the 1mm scribed width, hence the width we use in the following calculations is 0.66mm. The room temperature resistivity of the annealed film was  $8.0 \times 10^{-7} \Omega\text{-m}$ , which is about four orders of magnitude lower than the unannealed film. However, the resistivity is between one and two orders of magnitude greater than the resistivity of bulk gold which is  $2.02 \times 10^{-8} \Omega\text{-m}$  at 273K (Meaden 1966).

Figure 2 shows the resistivity of the annealed film as a function of temperature. The resistivity drops almost linearly from  $8.0 \times 10^{-7} \Omega\text{-m}$  at room temperature to  $4.9 \times 10^{-7} \Omega\text{-m}$  at 30K, below which it becomes virtually temperature independent. The residual resistance ratio (RRR), define as  $\rho_{273}/\rho_4$ , is about 1.6 and is much smaller than the values between 100 and 1000 found for other gold films (Sambles et. al 1982, de Vries 1987). The low RRR indicates that the films are disordered and that elastic scattering of the electrons is strong. The resistivity of the film can be written as the sum of two components,

$$\rho = \rho_i + \rho_p(T)$$

where the resistivities  $\rho_i$  and  $\rho_p(T)$  are due to impurity and phonon scattering, respectively. Taking the low temperature resistivity to be  $\rho_i$ , and assuming the electron density to be that of gold, using the Drude formalism we estimate the mean-free-path for electron elastic scattering to be about 1.8nm. This length scale is close to the size of the naked 55 atom gold cluster, which has been shown to be in the range 1.3-1.4nm (Schmid et. al 1988). The similarity between the



elastic scattering length and the cluster diameter suggests that the electron elastic scattering is caused by the physical size of the gold cluster. The temperature dependent resistivity  $\rho_p(T)$  due to electron-phonon scattering can be approximated using the Bloch-Gruneisen formula (Ziman 1960)

$$\rho_p = \rho_1 \left(\frac{T}{\Theta}\right)^5 J_5\left(\frac{\Theta}{T}\right)$$

where  $\Theta$  is the Debye temperature,  $\rho_1$  is a constant, and  $J_5(x)$  is the Debye integral given by,

$$J_5\left(\frac{\Theta}{T}\right) = \int_0^{\frac{\Theta}{T}} \frac{z^5 e^z dz}{(e^z - 1)^2}$$

With  $\Theta = 160\text{K}$ , a good fit to the data is obtained with  $\rho_1 = 6.12 \times 10^{-7} \Omega\text{-m}$ , as shown by the dashed line in Fig.2.

Disordered metal films are known to exhibit resistance corrections at temperatures where the electron diffusion length  $\ell = (D\tau)^{1/2}$  becomes greater than the film thickness (Thouless 1977). Here the electron diffusion constant  $D = \frac{1}{2} v_F^2 \tau_e$ , where  $\tau_e$  is the elastic scattering time and  $v_F$  is the Fermi velocity which we take to be that of bulk gold. The other symbols have their usual meaning. We estimate that  $\ell = 74\text{nm}$  at the lowest temperature used, 1.4 K. Therefore, since we do not see resistance corrections in the films down to the lowest temperature studied, the film thickness must be greater than or comparable to 74nm. To within the accuracy to which we know the various parameters in the diffusion length, this argument is consistent with the

notion that the film thickness is of the order of the grain size which we estimate from the micrographs (Fig. 1b) to be approximately 60nm.

### 3.2. Electron beam direct writing

Test patterns for different electron-beam doses are shown in Fig.3. Well defined 0.1  $\mu\text{m}$  lines are obtained with a dosage of about  $100\text{nCcm}^{-1}$  and an electron accelerating voltage of 40kV. Below this dosage the test patterns became discontinuous. To facilitate electrical measurements a four-terminal device was patterned at a dosage of  $100\text{nCcm}^{-1}$ , as shown in Fig.4. An EPMA analysis of this structure showed that the weight percentage of gold was 86% (Table 1) which is above that of the original gold compound film, but below the value obtained by thermal decomposition. The four-terminal structure was found to have an extremely high resistivity of greater than  $10^3\Omega\text{-m}$  at room temperature; that is, five orders of magnitude above the value for the thermally decomposed material. One possible explanation is that the organic ligand triphenylphosphine is trapped inside the gold compound and/or becomes cross-linked under electron beam exposure. Cross-linking would make the organic material insoluble in dichloromethane, therefore it would not be removed during development of the film. To investigate this hypothesis a solution of triphenylphosphine in dichloromethane/dichloroethane was spin-coated onto a silicon wafer. It was found that a triphenylphosphine film crystallized on the wafer after spinning. Nevertheless, after electron beam exposure and development, patterns were observed at about the same dosage level used to form the patterns with the gold cluster film. It is likely, therefore, that the triphenylphosphine ligand in the gold compound was cross-linked by the electron beam exposure so that they

could not be removed during development.

In an attempt to remove any organic residues, the films underwent chemical extraction, as described in the experimental section above. After this treatment the weight percentage of gold in the film was found to increase to 93% (Table 1). The morphology of the film did not appear to change after chemical extraction and the room temperature resistivity of the film remained very high. The failure of the chemical extraction is consistent with the supposition that the electron beam causes cross-linking to occur in the organometallic film.

Firing was carried out in order to achieve removal of cross-linked organic materials. Figure 5a is a micrograph of the device after firing at 500°C for 5min in the air. Discrete gold islands can be seen along the device. Heating the device at 500°C for 5min under oxygen environment did not cause a noticeably different grain growth, as shown in Fig.5b. Firing under vacuum gave a similar discrete gold granular film but with smaller islands. After these firing procedures, the EPMA analysis showed the gold weight percentage had increased to 98% indicating that more organic material had been removed from the film. We believe that because of the minimization of surface, grain boundary, and interface energies discrete gold islands were formed during the annealing process which obviously prevents conduction in the films.

#### §4. CONCLUSIONS.

In summary, we have described the fabrication of conducting gold films from a spin coated gold cluster film. After thermal decomposition and annealing, a granular gold film with resistivity of  $10^{-6}\Omega\cdot m$  is formed. A four-terminal low temperature resistivity measurement shows

a RRR that is much lower than found in gold films prepared in more traditional ways. The low value of the RRR indicates that the films are disordered, even after annealing. From the elastic scattering length of the electrons we believe that the disorder is associated with boundaries between the gold clusters. When the gold cluster film is exposed by an electron beam, fine structures as small as  $0.1\ \mu\text{m}$  can be patterned directly with a dosage of  $100\text{nCcm}^{-1}$ . Although the electron beam exposed structures were not conducting, the technique itself may be useful for making high atomic weight nanostructures for use, for instance, in x-ray lithography optical components.

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Table 1. Electron probe microanalysis showing weight percentage of the three major elements in the gold compound structures in all stages.

Materials	Au	P	Cl
Caculated from Molecular formula	75	16	8
Spin coated film	79	8	12
Thermally decomposed film	96	3	<1
Thermally decomposed film after annealing at 180°C	97	0	3
Electron beam exposed film	86	6	8
EB exposed film after chemical extraction	93	4	3
EB exposed film after firing at 500°C	98	1	<1

Captions of the figures.

Figure 1. Micrograph of a) thermally decomposed film showing the grain size in the order of 20nm, and b) the decomposed film after thermal annealing at 180°C for another hour showing the grain growth to be in the order of 50nm.

Figure 2. Resistivity versus temperature for the thermally decomposed film. The dashed line is the fit to the data.

Figure 3. Photograph of the test patterns. The dosages were 10, 25, 50, and 75nCcm<sup>-1</sup> for the upper four groups from left to right with first two groups did not show up. The lower four groups were all written with line dosage of 100nCcm<sup>-1</sup>. Each group has four line structures with linewidth of 10, 10, 50, and 100nm from top. In each case the 10nm lines were not found.

Figure 4. SEM micrograph of the electron beam exposed four-terminal device.

Figure 5. SEM micrograph of the electron beam exposed film after a) firing in the air at 500°C for 5 minutes and b) further heating at same temperature but in the oxygen environment for another 5 minutes.



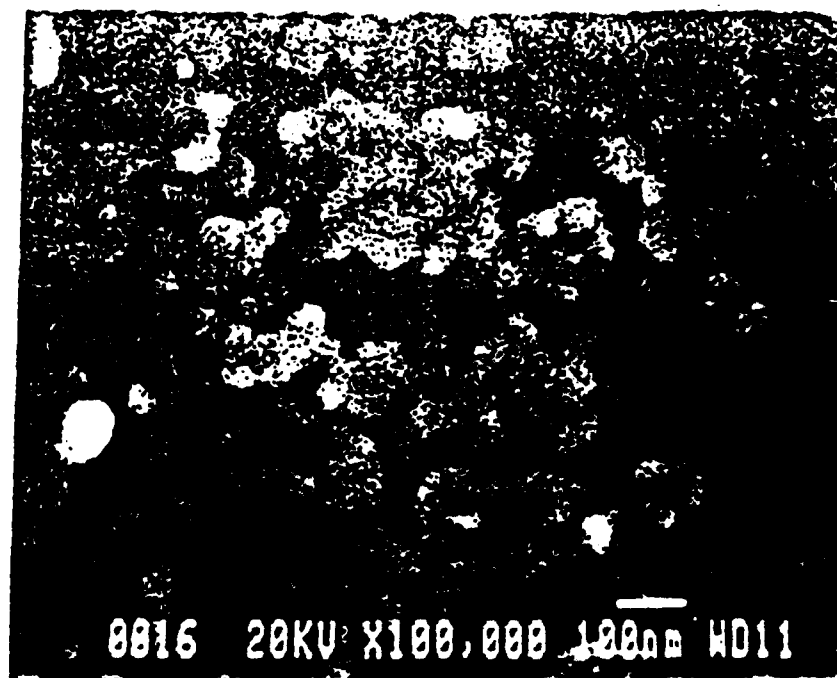


Fig 1b

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Fig. 1a

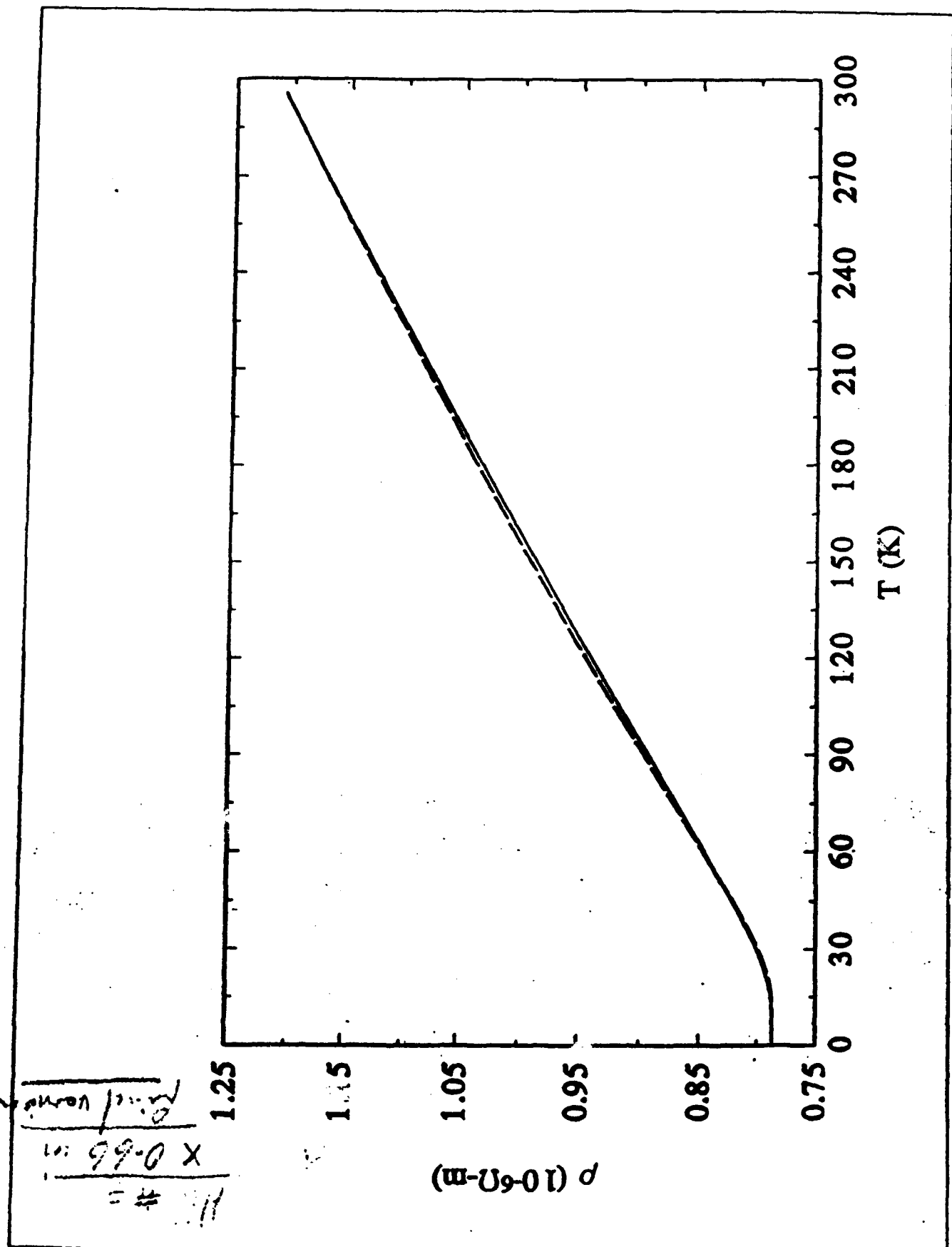


Fig. 2

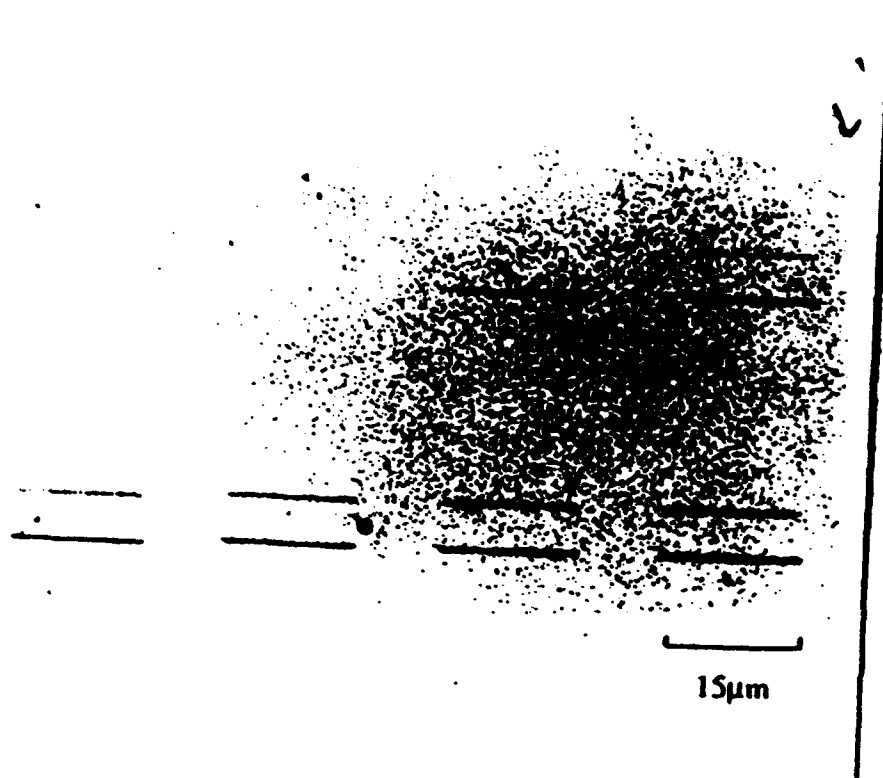


Fig. 3

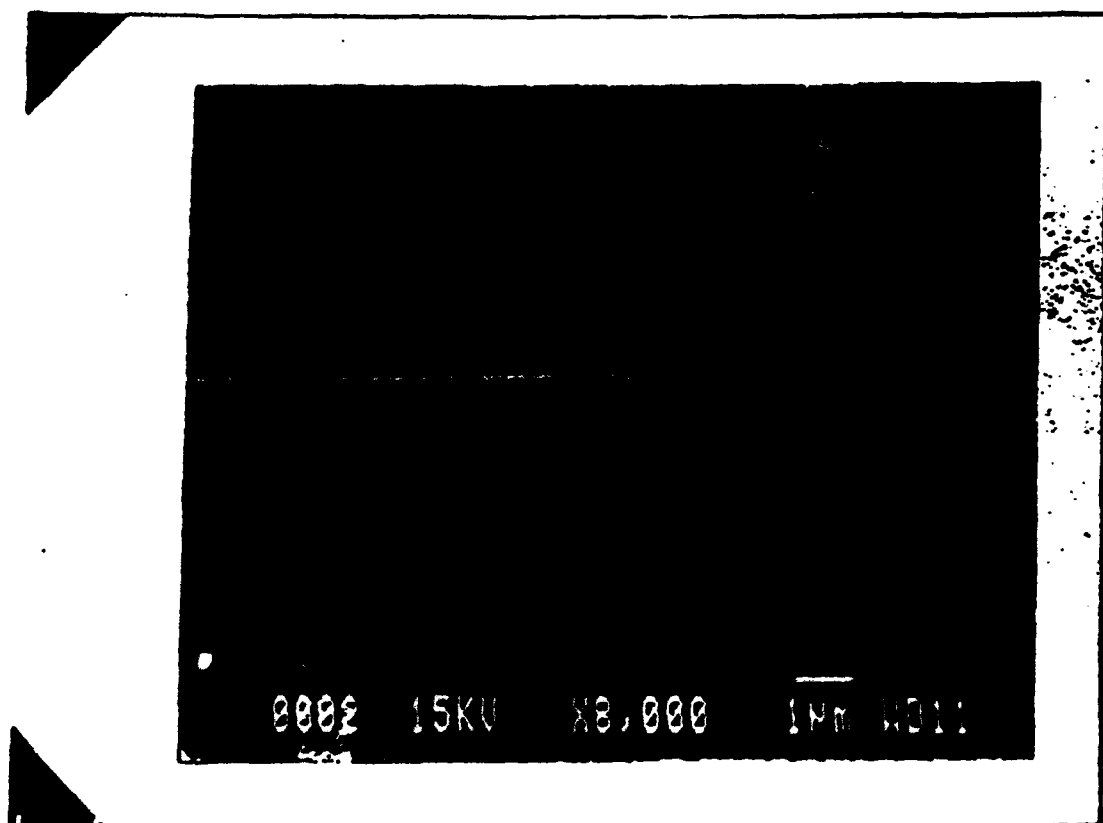


Fig. 4

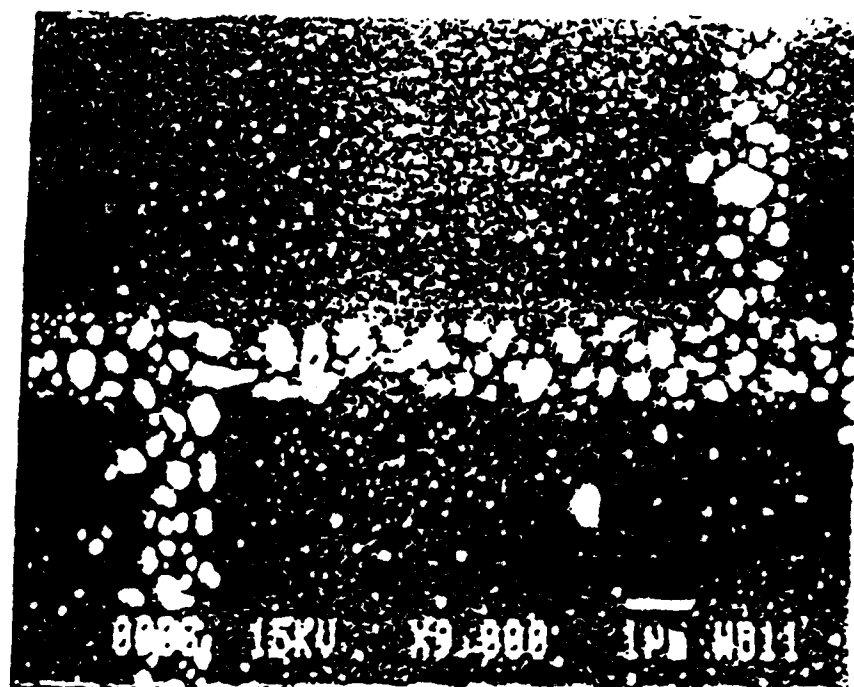


Fig. 5a

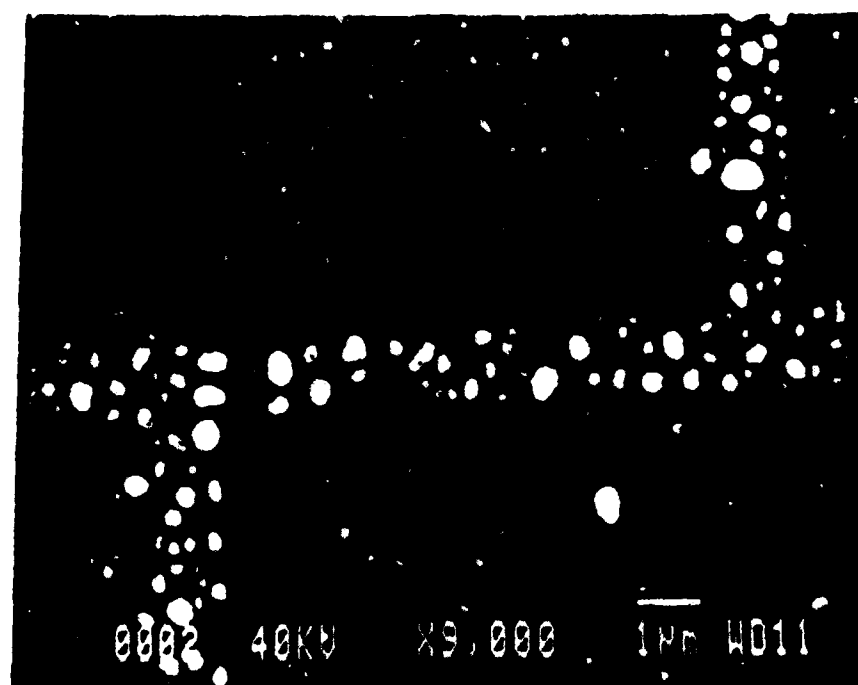


Fig. 5b